

EVOLUTION AND REMOVAL OF POLLUTANTS FROM THE GASIFICATION
OF A SUBBITUMINOUS COAL IN A FLUIDIZED BED REACTOR

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INTRODUCTION

As a part of a continuing research program on the environmental aspects of fuel conversion, the U. S. Environmental Protection Agency has sponsored a research project on coal gasification at North Carolina State University in the Department of Chemical Engineering. The facility used for this research is a small coal gasification-gas cleaning pilot plant. The overall objective of the project is to characterize the gaseous and condensed phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants depend on adjustable process parameters.

A complete description of the facility and operating procedures is given by Ferrell et al., Vol I, (1980), and in abbreviated form by Felder et al. (1980). A schematic diagram of the Gasifier, the Acid Gas Removal System (AGRS), and other major components is shown in Figure 1.

In an initial series of runs on the gasifier, a pretreated Western Kentucky No. 11 coal was gasified with steam and oxygen. The results of this work are given by Ferrell et al., Vol II, (1981), and were presented at the EPA Symposium on Environmental Aspects of Fuel Conversion Technology V, held in St. Louis, Mo., September, 1980.

The second major study carried out on the facility was the steam-oxygen gasification of a New Mexico subbituminous coal (from the Navaho mine of the Utah International Co.) using refrigerated methanol as the AGRS solvent. This paper presents a brief summary of the gasifier operation using this coal, shows examples of analyses of some of the gasifier effluent streams, and presents a summary of the results of the operation of the AGRS using the gasifier make gas as feed.

SUMMARY OF GASIFIER OPERATION

The fluidized bed gasifier and raw gas cleaning system (cyclone, venturi scrubber, filters and heat exchanger) used for these studies was originally designed for the gasification of a devolatilized coal char with a very low volatile matter content. Extensive modification of the upper part of the gasifier, the venturi scrubber system, and the heat exchanger was required for operation with the high volatile matter New

Mexico coal. Table 1 shows an analysis of the char and coal used in studies to date. After modification, the system functioned well in providing a clean, dry gas to the acid gas removal system.

All of the experimental work so far has been carried out with the solid coal particles fed into the reactor several feet above the top of the fluidized bed. The particles are thus in contact with the hot product gases for several seconds before mixing into the fluidized bed, a mode of operation that tends to maximize the production of tars and other organic liquids from the coal. It is an excellent mode of operation for our present purpose since it produces relatively high concentrations of environmentally important elements and compounds.

TABLE 1
COAL AND CHAR ANALYSIS

	Coal Char	New Mexico Coal
<u>Proximate Analysis</u>		
Fixed Carbon	86.0	42.0
Volatile Matter	2.4	35.4
Moisture	0.9	10.5
Ash	10.7	22.6
<u>Ultimate Analysis</u>		
Carbon	83.8	52.5
Hydrogen	0.6	4.8
Oxygen	2.2	18.3
Nitrogen	0.1	1.2
Sulfur	2.6	0.6
Ash	10.7	22.6

A total of 15 gasifier runs were made covering a range of reactor parameters. For this series of runs, the average temperature of the fluidized bed was varied from about 1600°F to 1800°F, and the molar steam to carbon ratio was varied from about 1.0 to 2.0. The coal feed rate and the reactor pressure were kept nearly constant. Several of the first reactor runs were made with mixtures of coal and char, but all integrated runs reported on later were made with 100% coal. At the lower temperatures the production of methane and of tars and other hydrocarbons is maximized. As the temperature is increased, the make gas rate increases, the production of methane and other hydrocarbons decreases, and the concentration of CO₂ increases.

GASIFIER MODELING RESULTS

To aid in the formulation of gasifier performance correlations, a simple model has been developed which considers the gasification process to occur in three stages: instantaneous devolatilization of coal in a zone above the fluidized bed, instantaneous combustion of carbon at the

bottom of the bed, and steam-carbon gasification and water gas shift reaction in a single perfectly mixed isothermal stage. The model is significant in and of itself, but its particular importance to the project is that it enables the specification of gasifier conditions required to produce a feed to the acid gas removal system with a predetermined flow rate and composition.

In a previous report (Ferrell et al., 1981), the structure of the model was presented, and the ability of the model to correlate data on the gasification of a devolatilized bituminous coal was demonstrated. The model was subsequently extended to include the evolution of volatile gases in the pyrolysis stage of the gasification process, and used to fit the data from the present series of runs with the New Mexico subbituminous coal. The model takes as input the average reactor bed temperature and pressure, the bed dimensions, feed rates of coal, steam, oxygen, and nitrogen, solids holdup in the bed, and ultimate analysis of the feed coal, and calculates carbon conversion and make gas flow rate and composition. A complete description of the model in its present form will be given in an EPA report now in preparation. A lot of model predictions vs measured values of carbon conversion is shown in Figure 2. The reasonably close proximity of most points to the 45 degree line on this and similar plots for total make gas flow rate and individual species (CO , H_2 , CO_2) emissions is gratifying in view of the simplicity of the model.

AGRS OPERATION AND RESULTS

Top feeding coal into the gasifier allows a substantial amount of devolatilization to take place before the coal enters the fluidized bed. While most commercial fluidized bed gasifiers will use a deep-bed injection method of feeding coal into the fluidized bed, it was decided not to modify our system in order to maximize the formation of tars, oils, and other hydrocarbons and to provide a more complete test of the AGRS.

It should also be noted that the relatively simple acid gas removal system used in this study lacks the complexity of the selective systems found in many physical absorption processes. These systems, which use more than one absorber and stripper, and often several flash tanks, separate sulfur gases from carbon dioxide before further processing of the acid gas. This is done to concentrate the sulfur gases before they are fed to a sulfur recovery unit, and to recover the CO_2 or vent the CO_2 -rich stream to the atmosphere. While the AGRS used in this study could have been modified to emulate an existing selective absorption process, it was decided that data obtained from a relatively simple but well-characterized system would be of more use than data obtained from a fairly complex system, similar but not identical, to existing commercial systems. Through judicious use of computer simulation and engineering calculations, the data obtained from our system should be extrapolatable to more industrially significant situations.

Complete results from all runs carried out will be published in a forthcoming EPA report. Illustrative results from a single run will be presented here. Gas analyses from the six different locations shown in Figure 1 are given in Table 2. The paragraphs that follow summarize the principal conclusions derived from analyses of the run data.

TABLE 2
GAS ANALYSIS SUMMARY FOR AMI-57/GO-76

Species	Sample Train	PCS Tank	Sour Gas	Sweet Gas	Flash Gas	Acid Gas
H ₂	31.60	31.11	31.29	42.38	15.58	0.00
CO ₂	23.51	23.91	21.98	-----	25.99	64.74
C ₂ H ₄	0.52	0.53	0.56	0.0242	1.28	1.54
C ₂ H ₆	0.72	0.72	0.76	0.0164	1.92	2.13
H ₂ S	0.250	0.284	0.287	0.0048	0.090	0.66
COS	0.0078	0.0076	0.0076	0.0001	0.0041	0.027
N ₂	19.36	19.61	19.93	26.79	19.27	23.06
CH ₄	6.56	6.46	6.57	7.54	14.20	2.36
CO	17.29	17.47	17.92	23.35	21.55	1.80
Benzene	0.087	0.097	0.234	TRACE	0.0031	0.15
Toluene	0.031	0.034	0.534	0.0054	0.0033	0.030
Ethyl Benz.	0.0016	0.0017	0.0450	-----	-----	-----
Xylenes	0.0080	0.0094	0.1557	-----	-----	-----
Thiophene*	44	44	127	-----	-----	-----
CH ₃ SH*	16	29	28	TRACE	5	TRACE
C ₂ H ₅ SH*	TRACE	-----	8	-----	-----	-----
CS ₂	TRACE	3	TRACE	TRACE	TRACE	TRACE
Propylene*	1505	1521	1811	107	995	4640
Propane*	208	198	253	301	172	2203
Butane	185	150	143	54	91	71
Methanol**	-----	-----	-----	-----	-----	3.68

* Parts per Million (volume)

** Estimated

Acid Gas Removal

The primary function of the AGRS is to remove CO₂ and sulfur compounds from the gases produced during coal gasification. When using refrigerated methanol, the absorber also acts as an excellent trap for any other compound which condenses or dissolves in the methanol at absorber conditions.

The run data show that for the range of conditions studied, the most significant factor in high acid gas removal efficiencies is stripping efficiency. With the use of more extreme operating conditions and "cleaner" methanol fed to the absorber, the levels of CO₂, COS and H₂S in the sweet gas can be reduced to acceptable levels. This is a particularly important point in the case of COS removal which poses

problems for many coal gas cleaning systems. The data show that refrigerated methanol is effective in removing COS and no unusual solubility characteristics were evident at moderate pressures and low liquid temperatures.

Trace Sulfur Compounds

There are several sulfur compounds besides H_2S and COS present in the gas fed to the AGRS which must be removed. Table 2 shows the distribution of several of these compounds in the AGRS. While there is some scatter in the analyses for methyl mercaptan, thiophene, CS_2 , and ethyl mercaptan/dimethyl sulfide, it appears that in most runs they are removed to very low levels in the absorber.

A point of potential environmental significance is that while these compounds are removed to low levels, they are not completely accounted for in the flash and acid gas streams. This can be seen for methyl mercaptan and thiophene, which are present in relatively high levels in the feed gas. These compounds will accumulate in the recirculatory solvent and most likely eventually leave the system in one of three exit streams: sweet gas, flash gas, or acid gas. Because most sulfur recovery systems cannot treat mercaptans and thiophene, they will present emission problems if some additional method of treating these gases is not used. This can be a significant problem because the total sulfur from mercaptans, organic sulfides, CS_2 , and thiophene is approximately half of the total sulfur associated with COS. If these compounds appear with the sweet gas, they are likely to affect adversely downstream methanation catalysts. The presence of these compounds in the sweet gas stream is also a problem if the gas is to be burned for immediate use because the sulfur in these compounds will be converted to SO_2 .

In examining the results from all runs, there appears to be some pattern of trace sulfur species distribution. An increase in stripper temperature from $-5.6^\circ F$ to $48^\circ F$ resulted in substantially greater amounts of mercaptan and thiophene in the acid gas stream. CS_2 seems to distribute to all exit streams in most of the runs despite the differences in process conditions.

Perhaps the most significant finding here is that over a wide range of processing conditions, the presence of at least small amounts of several different sulfur species is to be expected in all AGRS exit streams, and provision must be made for handling the associated problems.

Aliphatic Hydrocarbons

As the amount of volatile matter present in a particular coal increases, the production of aliphatic, aromatic, and polynuclear aromatic compounds produced during gasification also increases. Over the range of conditions studied here, the most significant point to be made about the distribution of aliphatic hydrocarbons is their presence in significant quantities in the flash and acid gases. Although flashing of

the methanol down to atmospheric pressure prior to stripping would release most of the hydrocarbons, the CO₂-rich flash gas would still contain substantial amounts of several hydrocarbon species. This stream would require further processing before it could be vented.

In a run in which the gasifier was operated at a lower temperature to increase the production of hydrocarbons, the aliphatics (excluding methane) made up almost 4.5% of the acid gas stream and 3.5% of the flash gas stream. While staging the flashing operations may result in a better distribution of these compounds, the total product from the flashing and stripping operations must be either recovered as product, fed to a sulfur recovery unit, or vented to the atmosphere. Since it is unlikely that all of the aliphatic hydrocarbons will appear in the sweet gas stream, as evidenced by the data collected here, additional treatment will be necessary to prevent their eventual appearance in a vent stream.

There appears to be no unusual pattern of distribution of aliphatic hydrocarbons in the AGRS. The lighter hydrocarbons-- methane, ethylene, and ethane-- seem to distribute as would be indicated from an examination of their pure-component solubilities in methanol. The magnitude of their solubilities, however, are greater than would be expected from Henry's law, especially at the high pressures used in the absorber. This is evident from the lower than predicted levels of ethane and ethylene in the sweet gas in several of the runs.

Aromatic Hydrocarbons

Because large amounts of aromatic hydrocarbons are produced during coal gasification, the potential for environmental problems is great. These compounds, which range from benzene to polynuclear species of many forms, must be prevented from escaping from the gas cleaning process and their distribution throughout the gas cleaning system is of great concern.

The simpler aromatics, benzene, toluene, and xylene, typically make up 0.1% (by volume) of the gas stream entering the AGRS. (See Table 2.) Analyses performed for selected runs indicate that significant quantities of these compounds are found in the solvent leaving the stripper. Eventually these compounds would build up in the solvent to the point of saturation. If the solvent is not effectively purged of these compounds periodically, they would begin to appear in several of the process streams.

Methanol Analysis

In order to identify the various hydrocarbon species that accumulate in the methanol, samples of the methanol leaving the stripper were taken for several runs. These samples were then analyzed by gas chromatography/mass spectrometry. The compounds detected are shown in Table 3. The presence of several siloxanes and phthalates was probably related to some contamination of the sample during processing.

Results from these runs indicate that most of the compounds accumulating in the methanol are simple aromatics, primarily substituted benzenes. A few C₁₀ and C₁₁ isomers were identified, indicating that naphthalene is probably present but at trace levels. The presence of trace amounts of C₁₄ and C₁₅ isomers were found in but they could not be better identified.¹⁴ These may be polynuclear aromatics but they were present in very small amounts relative to the simpler aromatics.

Samples of liquid condensing in the knockout tank downstream from the sour gas compressor were collected and analyzed by GC/MS. This condensate contains most of the heavier hydrocarbons fed to the AGRS. Results of these analyses are presented in Table 4, and show that the compounds identified are very similar to those found in the stripped methanol. Again, mostly simple aromatics were found. No polynuclear aromatics were present, which supports the findings of the earlier analyses.

Results from these analyses indicate that very little, if any, polynuclear aromatic compounds were present in the gas fed to the AGRS. This is a particularly important finding. Analyses of the water used to quench the gasifier product gas stream showed that a substantial amount of polynuclear aromatics were present. Evidently, scrubbing of the raw product gas with water effectively removes these compounds.

Although polynuclear aromatics are removed by the quenching process, substantial amounts of simpler aromatics will be present in the sour gas fed to the AGRS. The use of cold traps may remove some of these compounds but provision must be made to prevent their release to the atmosphere through vent streams or through the sulfur recovery unit. The accumulation of these compounds in the methanol further complicates the problem because of the increased likelihood of their distribution to a number of process streams. Achieving efficient solvent regeneration is, therefore, a key step in avoiding environmental problems.

SUMMARY

A cyclone, a cold water quench scrubber, and a refrigerated methanol absorber have been used to clean the make gas from the steam-oxygen gasification of a New Mexico subbituminous coal in a pilot-scale fluidized bed reactor. A model developed for the gasifier provides the capability of predicting the make gas amount and composition as a function of gasifier operating conditions. The methanol functioned effectively for acid gas removal. Removal of CO₂, COS, and H₂S to sufficiently low levels was achieved with proper choice of operating conditions and effective solvent regeneration.

TABLE 3

COMPOUNDS IDENTIFIED IN STRIPPER EXIT METHANOL		
1. sat'd hydrocarbon	21. toluene	42. C ₃ alkyl benzene
2. CO ₂	22. methyl thiophene isomer	43. C ₃ alkyl benzene
3. C ₄ H ₈ isomer	23. C ₈ H ₁₆ isomer	44. C ₁₀ H ₂₂ isomer
4. tetramethylsilane	24. C ₈ H ₁₆ isomer	45. C ₁₀ H ₂₂ isomer
5. trichlorofluoro-methane	25. C ₈ H ₁₆ isomer	46. C ₄ alkyl benzene
6. C ₅ H ₁₀ isomer	26. C ₈ H ₁₆ isomer (trace)	47. C ₁₀ H ₂₂ isomer
7. unknown	27. C ₈ H ₁₄ isomer (trace)	48. C ₁₀ H ₂₀ isomer
8. Freon 113	28. hexamethyl cyclotrisiloxane	49. unknown hydrocarbon
9. cyclopentadiene	29. C ₉ H ₂₀ isomer	50. C ₉ H ₁₀
10. C ₆ H ₁₂ isomer	30. C ₉ H ₁₈ isomer	51. C ₉ H ₈ isomer
11. C ₆ H ₁₄ isomer	31. ethyl benzene	52. alkyl benzene isomer
12. C ₆ H ₁₀ isomer	32. xylene (M,P)	53. C ₁₁ H ₂₄ isomer
13. benzene	33. styrene	54. C ₈ H ₁₀ isomer
14. C ₇ H ₁₄ isomer	34. xylene (O)	55. C ₁₁ H ₂₄ isomer
15. C ₇ H ₁₆ isomer	35. C ₉ H ₁₈ isomer	56. C ₈ H ₁₀ isomer
16. C ₇ H ₁₆ isomer	36. C ₉ H ₂₀ isomer	57. unknown siloxane
17. C ₇ H ₁₂ isomer	37. C ₃ alkyl benzene	58. unknown siloxane
18. C ₇ H ₁₂ isomer	38. C ₁₀ H ₂₂ isomer	59. unknown siloxane
19. C ₇ H ₁₂ isomer	39. unknown hydrocarbon	60. C ₁₄ H ₃₀ isomer
20. unknown hydrocarbon	40. unknown hydrocarbon	61. C ₁₄ H ₃₀ isomer
	41. C ₁₁ H ₂₄ isomer	62. unknown
		63. C ₁₅ H ₃₂ isomer

TABLE 4

COMPOUNDS IDENTIFIED IN COMPRESSOR KNOCKOUT SAMPLE	
1. 1-pentene	10. substituted benzene
2. hydrocarbon	11. C ₈ hydrocarbon
3. benzene	12. C ₉ hydrocarbon
4. hydrocarbon	13. propyl or ethyl methyl substituted benzene
5. Toluene	14. propyl or ethyl methyl substituted benzene
6. cyclo C ₄ -C ₅	15. 1-decene
7. hydrocarbon	16. 2-propyl benzene
8. ethyl benzene	17. 1-ethyl-4-methyl benzene
9. dimethyl benzene	

The presence of several trace sulfur compounds--mercaptans, thiophenes, organic sulfides, and CS_2 --complicates the gas cleaning process because these compounds were found to distribute among all exit streams from the AGRS. Since no provision is made to specifically treat these forms of sulfur, the possibility of their emission into the atmosphere exists and must be dealt with to avoid significant environmental problems.

A wide variety of aliphatic and aromatic hydrocarbons are present in the gas stream fed to the AGRS. The aliphatic hydrocarbons, ranging from methane to butane, cover a wide range of solubilities. Their presence in all AGRS streams must be anticipated to prevent their emission to the atmosphere.

While a wide range of simple aromatics were identified in the gas stream fed to the AGRS, essentially no polynuclear aromatic compounds were found. Apparently, the water quenching process effectively removes these compounds from the gasifier product gas. However, significant quantities of simple aromatics were found to accumulate in the recirculating methanol, indicating a potential for their eventual discharge to the atmosphere. Provision must be made to periodically purge the solvent of these compounds and/or remove them prior to the AGRS through cold traps.

REFERENCES

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Figure 2
 Predicted vs. Experimental Carbon Conversion,
 Gasification of New Mexico Coal

